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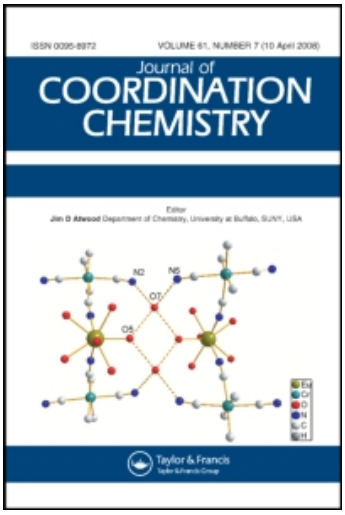

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Reactions of Copper(II) Complexes of Polydentate 8-Mercapto-Quinoline Derivatives with Phenols

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REACTIONS OF COPPER(II) COMPLEXES OF POLYDENTATE 8-MERCAPTO-QUINOLINE DERIVATIVES WITH PHENOLS

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The reactions of copper complexes with chelate thiaaza ligands as models of the active centres of 'blue' copper proteins have been studied. The overall reaction stoichiometry for the reduction of copper(II) complexes by 4-methyl-2,6-di-*tert*-butylphenol as well as hydroquinone in acetonitrile was found to be 2:1. The reactions are first-order with respect to the concentration of both complex and phenol. The second-
order rate constants and activation energies have been determined and the influence of ligand structure on these parameters discussed. The effect of pyridine in the reaction mixture on the redox potential and catalytic properties of some complexes on the oxidation of phenols by dioxygen was observed.

Keywords: Polydentates, mercaptoquinoline, copper(I,II), phenols, redox chemistry

INTRODUCTION

Spectroscopic and redox behaviour of copper(II) complexes with polydentate derivatives of 8-mercaptoquinoline[1] imitates the unusual properties of active centres of 'blue' copper proteins which act as biooxidants and electron carriers.[2] Recently, the oxidation of glutathione by these complexes has been studied.[3] The results obtained allow us to consider the complexes not only as structural but also as functional biomimetic models. Reaction with phenols is another example of oxidation properties of these copper(II) complexes.

The significance of the oxidation of phenols is difficult to estimate with respect to the different roles of phenols in the biosynthesis of natural phenolic compounds (alkaloids, pigments, lignins, antibiotics) and to the role of phenols as antioxidants. Phenols are subject to oxidative coupling (dimerization or polymerization), to monooxygenation (hydroxylation and formation of quinones) and to dioxygenation (cleavage of aromatic rings in catechols).

In natural processes, the copper-containing enzymes tyrosinase and laccase[2] participate in the oxidation of monophenols as well as diphenols. For modelling of the enzymatic reactions there have been used both simple copper salts[4,5] and complexes.[6,7] It follows from these studies that the nature of the ligand around the copper atom alters the catalytic activity of the complex. Phenol oxidation products

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depend markedly on reaction conditions but not on the structure of the catalyst.[6] However, kinetic data needed for proposal of reaction mechanisms are rather rare.

The aim of this paper is the kinetic analysis of the reactions of some models of 'blue' copper protein active centres with phenols. Five copper complexes with ligands L1 to L5 and two phenols, 4-methyl-2,6-di-*tert*-butylphenol (I), a commercially produced antioxidant, and hydroquinone (II) were chosen for the study.

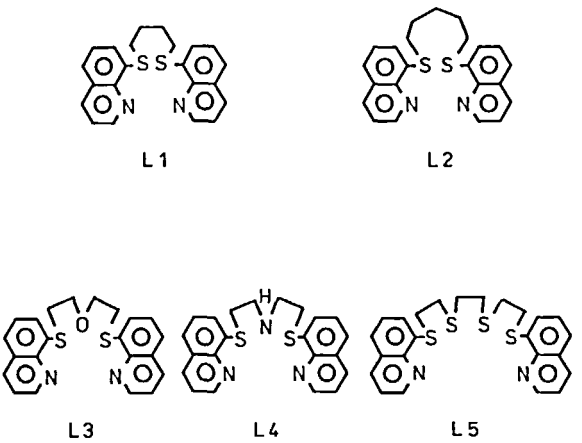

FIGURE 1

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EXPERIMENTAL

The $CuL(ClO_4)_2$ complexes were prepared as described previously.[1] 4-Methyl-2,6-di-*tert*-butylphenol from Juraj Dimitrov Chemical Works (Bratislava) and hydroquinone of analytical reagent grade (Lachema, Brno) were used without further purification. The solvent used was acetonitrile (Laborchemie, Apolda) because the complexes under study do not decompose and spontaneously reduce in this solvent. The reaction kinetics were studied by conventional mixing experiments which were followed spectrophotometrically with a Specord UV-VIS apparatus (Zeiss, Jena). The kinetics were monitored at wavelengths where copper(II) species absorbed most strongly.

The voltammetric measurements were performed with a Polarographic Analyzer (PA 4, Laboratorní přístroje, Prague) with a three electrode arrangement. A platinum disc electrode was used as the working electrode, a calomel electrode with aqueous 4 M LiCl and a salt bridge filled with 0.1 M $NaClO_4$ in acetonitrile was employed as the reference electrode and platinum as auxiliary electrode. The supporting electrolyte was 0.1 M $NaClO_4$. Anaerobic experiments were made in an argon atmosphere.

RESULTS AND DISCUSSION

Reaction course and stoichiometry

In preliminary experiments we followed the reaction of CuL^{2+} complexes with

phenols I and II, with 2,4-dinitrophenol (III), 2,4,6-tribromophenol (IV), 2,4,6-trinitrophenol (V), 1-naphthol (VI), 1-nitroso-2-naphthol (VII) and 8-hydroxyquinoline (VIII). The reaction with phenols I, II, VI and VII, respectively, was expressed in the decrease in absorbance of the most characteristic absorption band of CuL^{2+} occurring within the region $\lambda_{max} = 630$ to 720 nm (Table I). This spectral change indicates the reduction of copper(II) to copper(I).[1] The spectrum of the reaction systems with phenols I, II and VIII shows one isobestic point in the region 450 to 500 nm during the CuL^{2+} redox change. After the addition of phenol VI, the CuL^{2+} absorbance at 550 nm at first increases and then decreases.

TABLE I

Redox potentials and parameters of the characteristic absorption bands of CuL^{2+} complexes in acetonitrile (0.1 M $NaClO_4$) in the absence and presence of pyridine.

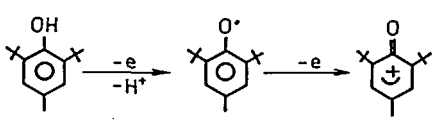
	without pyridine			with pyridine		
Complex	$E_{1/2}$[a]	ΔE_p[b]	$\lambda_{max}(\varepsilon)$[c]	$E_{1/2}$[a]	ΔE_p[b]	$\lambda_{max}(\varepsilon)$[c]
$CuL1^{2+}$	0.615	0.110	640(330)	0.240	0.380	602(100)
$CuL2^{2+}$	0.640	0.100	793(200)	0.275	0.170	660(40)
$CuL3^{2+}$	0.440	0.095	720(440)	0.280	0.300	620(50)
$CuL4^{2+}$	0.480	0.100	650(290)	0.270	0.200	625(60)
$CuL5^{2+}$	0.530	0.100	630(200)	0.285	0.270	590(55)

[a] $E_{1/2} = 1/2(E_{p.c} + E_{p.a})$; potentials were recorded *vs* 4 M LiCl SCE (+0.23 V *vs* NHE) at 22°C and are uncorrected for junction potential effects; the error is ± 5 mV. [b] $\Delta E_p = E_{p.a} - E_{p.c}$ for a scan rate of 0.1 V s^{-1}. [c] λ_{max} in nm and ε in $M^{-1}cm^{-1}$.

The addition of phenols with three substituents (which have −I effect; IV and V) leads to a red shift and to increase in intensity of the CuL^{2+} characteristic absorption bands. On the basis of this the rapid formation of relatively stable CuL^{2+} adducts with phenols IV and V may be assumed, as was the case with the CuL^{2+} reaction with glutathione.[3] Phenols III and VII cause a large-scale change of the CuL^{2+} spectrum. Furthermore, we studied the CuL^{2+} reduction by phenols with one aromatic ring, I and II, in more detail.

The spectrophotometric titration of all complexes has shown that 1 mol of phenol I or II reduces 2 mols of CuL^{2+} both in the presence and absence of air. This indicates the total stoichiometry as well as the fact that copper complexes with ligands L1 to L5 are not catalysts of phenol oxidation by air.

According to the literature[8,9] phenoxyl radical Ia is the oxidation product of phenol I, and this



I Ia Ib (*1*)

may disproportionate to the initial phenol and to methylenequinone. Strong oxidizing agents (Ce^{4+}, $IrCl_6^{2-}$) oxidize Ia to the phenoxonium ion Ib which binds a further phenol molecule at position 4 either by a C–O or C–C bond,[6,8] or binds oxygen and is changed to quinone.[6] The CuL^{2+} redox potential (Table I) is evidently quite enough for the two-electron oxidation of I.

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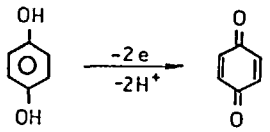
The reaction of hydroquinone to quinone is expressed by equation (*2*).



(*2*)

For this reducing agent the assumption of a two-electron oxidation is also fulfilled. Thus, the determined reaction stoichiometry corresponds with the equations (*1*) and (*2*). The rate-determining steps may, however, be different.

Reaction kinetics

Kinetic measurements were performed at different ratios of the initial concentrations of CuL^{2+} and phenols where the concentrations varied in the range 2×10^{-4}–8×10^{-4} M CuL^{2+}, 2×10^{-2}–2×10^{-1} M phenol I and 1×10^{-4}–2×10^{-2} M phenol II. The partial reaction order against the CuL^{2+} (α) and phenol (β) concentration was determined from the initial reaction rate, v_o

$$v_o = -\frac{1}{2}\left(\frac{d[CuL^{2+}]}{dt}\right)_{t \to 0} \qquad (3)$$

by the method of change of initial concentrations of reagents (the factor 1/2 incorporates the reaction stoichiometry). Thus in anaerobic as well as aerobic conditions there were found the values $\alpha = 1.0 \pm 0.3$ and $\beta = 1.0 \pm 0.2$ for all complexes. The error in the values α and β is connected with difficulties in the determination of v_o. The kinetic equation (*4*)

$$v = k_{obs}\,[CuL^{2+}]\,[\text{phenol}] \qquad (4)$$

was considered to be correct for all reactions.

Processing of time dependences of the CuL^{2+} concentration ($\ln[CuL^{2+}]$) *vs* time in the case of a great excess of phenol over CuL^{2+} or $\ln([\text{phenol}]/[CuL^{2+}])$ *vs* time in the case of comparable phenol and CuL^{2+} concentrations) gave straight lines (correlation coefficient $r = 0.980$–0.995) and thus confirmed the validity of equation (*4*), at least during the reduction of CuL^{2+} up to *ca* 90%. From the slopes, values of rate constants, k_{obs}, were determined (Table II).

Values of activation energy were calculated for data from 22.0 to 65.0°C. The linearity of dependences indicates a single reaction mechanism over the given temperature interval.

Attention is drawn to the difference in reaction rate of $CuL1^{2+}$ and other CuL^{2+} complexes as well as to the increase in E_a in the case of $CuL5^{2+}$. This indicates the transfer of electron density from the heteroatoms of the aliphatic chain of the ligand L due to which the electron transfer from phenol to copper is more difficult. Similar effects of the CuL^{2+} coordination sphere were observed in the reduction of these complexes by glutathione[3] which, however, involved intramolecular electron transfer within the CuL-glutathione intermediate.

The evaluation of kinetic measurements performed in the presence of oxygen has shown that the reduction of complexes by phenol I is faster than under anaerobic conditions. Thus, for example, the rate constant $k_{obs} = 16.7 \times 10^{-3}$ M^{-1} s^{-1}

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corresponds to the complex $CuL1^{2+}$ under aerobic conditions whereas under anaerobic conditions this value is $k_{obs} = 10.3 \times 10^{-3}\ M^{-1}\ s^{-1}$ (22°C). In the case of phenol II the reduction rate of CuL^{2+} was not changed substantially in the presence of oxygen.

TABLE II

Kinetic data for the reduction of CuL^{2+} by 4-methyl-2,6-di-*tert*-butylphenol (I) and hydroquinone (II) in acetonitrile under anaerobic conditions.

	Phenol I			Phenol II		
Complex	T (°C)	$10^3 \times k_{obs}$[a] ($M^{-1}s^{-1}$)	E_a[b] (kJ mol^{-1})	T (°C)	k_{obs}[a] ($M^{-1}s^{-1}$)	E_a[b] (kJ mol^{-1})
	22	10.3		22	202	
$CuL1^{2+}$	35	24.0	48.9	25	267	42.7
	44	41.3		33	542	
	52	65.2		38	837	
	35	8.0		22	5.1	
$CuL2^{2+}$	40	11.1	52.7	25	7.3	84.9
	52	23.4		33	17.9	
	64	47.0		40	37.6	
	35	9.0		22	1.4	
$CuL3^{2+}$	40	12.0	44.8	25	2.1	90.4
	52	22.5		33	5.4	
	64	40.4		38	9.6	
	35	5.5		22	1.7	
$CuL4^{2+}$	40	7.5	38.1	25	2.5	84.1
	52	15.5		33	6.0	
	64	30.1		40	12.7	
	35	2.5		22	3.7	
$CuL5^{2+}$	40	3.6	61.1	25	5.8	108.8
	56	11.5		28	9.0	
	64	19.4		38	36.1	

[a] The mean value of independent kinetic runs at 4 different concentrations of CuL^{2+} and phenols; uncertainty is ±20%. [b] Uncertainty is ±4 kJ mol^{-1}.

The influence of oxygen may be explained by the formation of an unstable Ic radical,[9] reaction (5),

Ia Ic (5)

which by recombination with phenoxyl Ia forms the quinolidic peroxide, or oxidizes a further molecule of phenol I to Ia and this rapidly reacts with CuL^{2+}.

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Effect of pyridine

The effect of the copper coordination sphere on the redox potential and kinetic parameters led us to investigate the CuL^{2+} reduction by phenols in a medium of stronger donor properties. For this we have used pyridine concentrations of 0.1 to 1 M. Under aerobic conditions thus prevented any decrease in $CuL1^{2+}$ and $CuL2^{2+}$ absorbance during reaction with phenol I. The reduction of Cu(II) complexes was observed only after an induction period; the reduction rate was near to that in the absence of pyridine. Increase in temperature shortened the induction period, but higher pyridine concentrations did not substantially alter it. By repeated introduction of oxygen into the CuL^{+} solution containing excess phenol I and pyridine, the absorbance increased and after a certain period decreased again. Thus oxygen changes copper(I) to copper(II) and the induction period is connected with consumption of oxygen. From this it follows that the CuL^{2+} complexes act in the presence of pyridine as catalysts of the oxidation of phenol I by oxygen. The CuL^{2+} reduction by phenol II is very fast and so the induction period in the presence of oxygen and pyridine was not observed. The effect of pyridine was not evident in the reaction of the complexes $CuL3^{2+}$ to $CuL5^{2+}$, and this also confirms the interaction of the copper atom with the heteroatom in the aliphatic chain of the ligand L.

From the data in Table I it can be seen that the redox potentials of the complexes $CuL1^{2+}$ and $CuL2^{2+}$ decrease in the presence of pyridine. The potential shift is, however, relatively small by comparison to the value of the redox potential recorded for $Cu(ClO_4)_2$ in the same medium (-0.58 V *vs* SCE). This indicates the preservation of the CuL^{2+} complexes and confirms the pyridine bond to the complex with an unsaturated coordination sphere. The change of electronic spectrum (Table I) does not show the expected red shift of the absorption band, but electronic spectra generally are not diagnostic of Cu(II) geometry. In spite of the fact that the redox potentials of the CuL^{2+} adducts with pyridine are high, CuL^{+} reoxidation by oxygen and catalysis of the reaction still seem to be possible.

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